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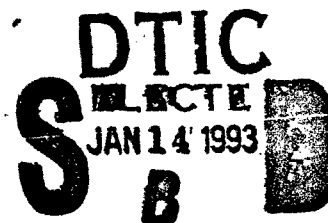
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## A Passive Badge Dosimeter for HCl Detection and Measurement

### PROJECT SUMMARY

The research conducted during this phase I SBIR project involved a thorough evaluation of the use of dye indicator molecules to provide a colorimetric detection of gas phase HCl molecules. A wide range of acid-base indicators, incorporated into a variety of physical (i.e., potential badge type) configurations were employed. These physical configurations included dye indicator incorporation into encapsulated micron sized liquid crystal droplets; adsorption on silica gel; incorporation into a polyvinyl alcohol thin film; and adsorption on the surface of thin film chromatography strips using a solvent evaporation procedure. Nine different acid-base dye indicators were selected and evaluated using these various sample preparation modes. In general, the acid-base dye indicators chosen for evaluation were selected on the basis of their  $pK_a$  values using indicators having values of  $\leq 7.0$ .

Samples of the various dye encoded materials described above were tested in our laboratories for sensitivity towards gaseous HCl. These tests were qualitative in nature in that they involved exposure of the dye indicator samples to vapors from solutions of varying concentration of hydrochloric acid. With the exception of the microencapsulated samples, all of the samples changed color when exposed to sufficiently high concentrations of HCl vapor. In general, detector sensitivity correlated with indicator  $pK_a$  with the highest sensitivity being noted for indicators with  $pK_a \sim 7.0$ . The microencapsulated dye/liquid crystal droplets exhibited no color changes even on exposure to vapors from concentrated HCl solutions. The lack of color change with these samples is attributed to poor permeability of the HCl molecules through the polymer membrane encasing the liquid crystal/indicator solution.

Quantitative measure of the dye indicator HCl sensitivity was obtained through measurements conducted by scientists at USABRDL. These tests involved exposure of the various dye encoded materials to a flow of  $N_2$  gas containing known HCl concentrations ranging from 50 to 1400  $mg/m^3$ . Both the thin layer chromatography and silica gel samples exhibited good HCl sensitivity, with the most sensitive samples undergoing noticeable color changes at HCl levels around  $\sim 55 mg/m^3$ . In general, the PVA dye containing thin films exhibited poor sensitivity to HCl requiring exposure to concentrated HCl vapors in order to achieve noticeable color change.

This phase I effort thus demonstrates the feasibility of fabricating relatively simple dye indicator type badges as passive dosimeters for monitoring gas phase HCl molecules. Although the phase I effort has demonstrated the general feasibility of this approach, the sensitivity of the badge developed must be significantly improved in order to meet Army needs in terms of threshold level value (TLV) specification. Using procedures outlined briefly at the end of this report, we feel that this enhanced sensitivity can be achieved within the framework of the dye indicator badges developed. Furthermore, attainment of improved sensitivity, along with the range of dye sensitivities noted in the phase I study, provides the obvious advantageous possibility of offering a range of HCl detection sensitivity within one single badge. This could be achieved by simply using several different dyes aligned along a TLC strip. These dyes could be chosen to cover a wide range of HCl concentration induced color changes. Such sensitivity enhancement and multi-HCl sensitivity development represents the basis for a phase II effort on this project.

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## Introduction

A need exists to monitor HCl exposure by military personnel. This is especially important for operators of military weapon systems which use perchlorate based propellants. These personnel are frequently exposed to short-term high concentrations of HCl. An accurate method of monitoring the extent of soldier exposure to HCl is required if much-needed correlations between adverse health effects and/or performance decrements from HCl exposure are to be developed.

A number of studies have been carried out to develop quantitative approaches to monitoring atmospheric HCl in areas involving rocket launching activities. The majority of these methods center on absorption spectroscopy, particularly infrared absorption (ref. 1-3). Whereas extreme sensitivity for HCl detection has been demonstrated (i.e., down to the few ppm range), these spectroscopic techniques are relatively cumbersome, expensive and non-portable in nature. These spectroscopic techniques in general require extensive calibration efforts and they are subject to a large variety of potential experimental breakdowns. In addition to spectroscopic measurements, techniques such as those employing piezoelectric crystal detectors (ref. 4) have been tested in terms of measuring low concentrations of HCl. Although good HCl sensitivity is available with such detectors, the quartz crystal type detection suffers from serious interferences from a variety of other atmospheric gases as well as from a general lack of portability. Again, extensive calibration and verification procedures are required to obtain quantitative estimates of atmospheric HCl concentrations.

Although analytical methods such as IR absorption spectroscopy can obviously provide precise and unequivocal determination of atmospheric HCl, the current need extends to the development of a reliable dosimeter badge-type detector which would be worn by military personnel. As in the case of radiation dosage monitoring, these badges would be read from time to time yielding the accumulated HCl exposure to that point. These HCl dosimeter badges must be lightweight and thus not obstruct in any way the activities of the wearer. Additionally, these dosimeters should be relatively inexpensive and thus disposable after use.

The purpose of the current SBIR phase I initiative was to explore a new approach to the development of a passive HCl dosimeter badge which would meet the above-mentioned criteria. The focus of this project centered on the use of color changes in acid-base dye indicators on exposure to gaseous HCl to signal the presence of HCl molecules in air samples. The rapidity and intensity of this color change would be expected to be a proportional function of the gaseous HCl concentration. The phase I work plan involved a thorough evaluation of this indicator approach to HCl monitoring. The research conducted included design and preparation of various physical approaches to be used in construction of the dye indicator encoded dosimeters. The various potential badge type designs identified were then employed to evaluate a wide variety of different candidate dye indicator molecules.

As documented in the results presented below, the use of appropriate acid-base indicators does indeed represent a potentially viable approach to the development of a passive HCl dosimeter badge which satisfies the previously identified criteria. Although the results obtained clearly support the feasibility of this approach, future studies are required to improve the badge sensitivity to meet desired Army TLV. Practical suggestions to achieving this increased sensitivity are included at the end of this report and they represent the focus of a phase II effort on this problem.

## **Experimental**

### ***Sample Preparation***

Four separate physical approaches were employed in preparing the dye indicator dosimeter samples. The first approach involved dissolution of dye molecules in various liquid crystals followed by encapsulation of the homogeneous liquid crystal/dye indicator solution with a thin plastic membrane. The basic technology employed in producing the microencapsulated droplets is similar to that developed by Polytronix for use in our polymer dispersed liquid crystal (PDLC) displays. Details of the manufacture and properties of these PDLC materials have been presented by Wu and Doane (ref. 5-7). For thermoplastics with high destructive melting temperatures, the

homogeneous solution is preferably made by first dissolving polymer and liquid crystal in a suitable solvent followed by simple solvent evaporation to obtain the solid PDLC material. Alternatively, the solid matrix can be obtained by UV irradiation of a suitable mix when dealing with a photocurable polymer material. Very recently (ref. 8), we have demonstrated that the droplet size obtained in the photocuring process is readily controllable in terms of varying the incident UV light intensity. We have shown that the diameter of the droplets formed can be varied from as small as 0.1 micron to sizes as large as 20 micron by simple variation of the intensity of the incident UV light.

The PDLC material obtained can be cast into various shapes and forms during the curing cycle. The most common type of product we have made is in the form of thin flexible films. For example, although our films are typically 5 mil in thickness, we have successfully fabricated films as thin as 1 mil.

Various aspects of the electro-optic properties of these displays have been presented by Wu and Doane (ref. 6-7) and these electro-optic properties are important for the proposed research. By proper matching of the refractive indices of the plastic matrix with that of the liquid crystals, the PDLC film can be converted from a light scattering to a transparent state. This is achieved by sandwiching the PDLC film between two indium-tin oxide (ITO) coated glass plates and applying a small potential to the plates. The overall optical performance of these displays depends on the relative values of the refractive index of the polymer matrix and the LC material.

The PDLC electro-optic response described above is what we refer to as "normal mode operation" and, until 1989, was the only mode available. However, Polytronix has recently developed a "reversed mode" PDLC display in which the droplets are transparent in the absence of an applied field but become light scattering when a field is applied (ref. 9). The reverse mode operation has been achieved by surfactant treatment of the polymer skin casing of the microdroplets to produce a homeotropic liquid crystal molecular alignment inside the droplets. This homeotropic alignment is obtained when the liquid crystal molecules employed are those that exhibit negative

dielectric anisotropy. Of particular significance with respect to this proposed phase I project, we have also demonstrated that dye molecules can be incorporated in the liquid crystal microdroplets and these dye molecules are employed in obtaining a color display.

Finally, we wish to point out that in addition to fabricating films containing uniformly dispersed microdroplets we are also able to synthesize discrete microencapsulated spherical droplets (ref. 10). These individual droplets can then be arrayed on a substrate for use in various electro-optic devices. We have devoted considerable time and effort to perfecting the manufacture of these encapsulated microdroplets and we feel that we are the leaders in this field. We have successfully demonstrated discrete microdroplet formation with a variety of casing skin polymeric materials (e.g., polyvinyl alcohol and polyacrylic acid) along with a wide range of entrapped liquid crystal molecules, including various dye molecules. We are currently developing a full-color flat panel display based on the use of these dye molecule microencapsulated liquid crystal droplets.

A second type of badge preparation involved a novel system in which the dye indicator molecules are incorporated directly into a thin plastic film without intermediate involvement of liquid crystal molecules. These samples were prepared using a blend of polyvinyl alcohol (PVA), water and indicator molecules. This blend was prepared in the following manner: 20 grams of PVA were added to 250 mL of deionized water and stirred at 80 °C for 2 hours during which time the PVA dissolved forming a clear solution. This homogeneous solution was then allowed to cool slowly to room temperature retaining its clear transparency at 25 °C. Five gram aliquots of this homogeneous PVA/H<sub>2</sub>O solution were used to dissolve 25 mg of various dye indicator molecules. The dye molecules were dissolved in the PVA/H<sub>2</sub>O solution at room temperature using constant stirring. The resultant blend of PVA:H<sub>2</sub>O:dye was then cast as a film by placing the solution on an aluminum foil and heating in an oven at 80 °C for 20 minutes. This produced a thin film of PVA containing evenly dispersed indicator dye molecules as evidenced by a uniform coloration of the films so attained.

A third type of dosimeter developed centered on physical adsorption of the indicator dye molecules on silica gel. These samples were prepared by dissolving 50 mg of the dye in 10 mL of methanol. In general, the dyes employed exhibited good solubility in  $\text{CH}_3\text{OH}$ . After addition of 10 grams of silica gel to this solution, the  $\text{CH}_3\text{OH}$  was allowed to evaporate at room temperature. The resultant solid sample consisted of dye molecules adsorbed uniformly on the tiny (micron sized) silica gel particles.

The fourth type of dosimeter constructed also involved physical dye absorption on a solid substrate, in this case a thin layer chromatography (TLC) strip. These samples were prepared by immersing the TLC strips in solutions consisting of 25 mg of dye dissolved in 5 mL of  $\text{CH}_3\text{OH}$ . Contact between the TLC strip and the solution was maintained for one minute. After this time period, the TLC strip was removed and allowed to dry by evaporation.

The major portion of the initial experimental effort centered on evaluation of the best dye indicator/liquid crystal combination to employ in constructing the microencapsulated liquid crystal/dye droplets. These experiments included systematic studies of a large number of dye indicators from the standpoint of identifying molecules which would have acceptable solubility in typical liquid crystal systems and, at the same time, exhibit good  $\text{HCl}$  sensitivity. In general, the compact relatively polar molecules employed as typical acid-base indicators do not exhibit good solubility in the long-chain, relatively non-polar molecules which constitute typical liquid crystal molecular systems. Solubility data on these acid-base indicators in commercially available liquid crystal mixtures are not available. As a result, systematic studies were undertaken to determine indicator solubility in the liquid crystals to identify the best candidates for incorporation into droplets for microencapsulation purposes.

A qualitative test for  $\text{HCl}$  sensitivity for the various types of dosimeters was carried out in our laboratories. This involved exposure of the samples to atmospheres above solutions of varying concentrations of hydrochloric acid. The time required for a noticeable color change in the indicator was measured. Quantitative measurements of the  $\text{HCl}$  dosimeter sensitivity was obtained



via cooperation with scientists at USABRDL. The following experimental details were provided by USABRDL personnel. In these experiments, known concentrations of HCl gas were generated by two different methods. The first method used a VICI gas calibrator and HCl permeation tubes and produced HCl concentrations up to 20 mg/m<sup>3</sup>. The second method used a toxic gas dilution system which contained two flow controllers. The flow controllers were employed to mix N<sub>2</sub> and HCl in known amounts and resulted in HCl concentrations ranging from about 50 to 1400 mg/m<sup>3</sup>. The gas composition values were analyzed by ion chromatography to confirm the metered flows. Initially, the samples were placed in a plexiglas container of approximate dimensions 4 in x 6 in x 12 in. This container had two openings fitted with a hose barb; one for the inlet of HCl and one for the outlet. In later studies, the tubing from the gas generation device was directed onto the dye/substrates using the plexiglas container. This latter method eliminated any question of adsorption of HCl onto the container walls at low levels.

## Results

Since the original focus of this project was to evaluate the use of microencapsulated dye indicators, our initial effort was concentrated on the fabrication of the required microcapsules. This involved testing a large number of dye indicator molecules with respect to their compatibility with liquid crystals (used in the microencapsulating process) as well as to their HCl sensitivity. A total of 11 dyes were evaluated and the results obtained are summarized in Table I.

Of the materials tested, only crystal violet exhibited both good solubility in the liquid crystals and rapid color change on exposure to vapors of concentrated HCl. In view of this result, the initial microencapsulated droplets were fabricated using crystal violet dye. These were obtained by dissolving the crystal violet in liquid crystals (ZLI-2806) followed by encapsulation with a PVA encasing membrane. The choice of PVA as the encasing substrate material was based on the relatively high polarity of the vinyl alcohol monomer in which HCl should exhibit good permeability.

**Table I**  
**Preliminary Test Results of Indicator Dye Solubility and**  
**HCl Sensitivity in Liquid Crystal Solvents**

Dye #	Compound	Solubility in Liquid Crystals	HCl Sensitivity
1.	Bromocresol green	Poor	Excellent
2.	Bromocresol green (sodium salt)	Poor	Excellent
3.	Bromocresol purple (sodium salt)	Poor	Excellent
4.	Bromophenol blue	Poor	Excellent
5.	Bromothymol blue	Poor	Excellent
6.	Crystal violet	Good	Excellent
7.	Methyl green	Poor	Excellent
8.	1,5-Diaminoanthraquinone	Good	Poor
9.	Leucomalachite green	Good	Poor
10.	GZ-1	Good	Poor
11.	PB-2	Good	Poor

Various samples of encapsulated droplets were synthesized in which mean droplet size was varied over the 1 to 15 micron range. This droplet size was controlled by varying the ratio of PVA to crystal violet/liquid crystal mix and/or by controlling the mechanical agitation rate employed in generation of the microdroplets. Additionally, the thickness of the encasing PVA polymer skin is controllable to a certain extent via these same variables.

These crystal violet dye encoded droplets were then evaluated with respect to HCl sensitivity. For this purpose, one inch square arrays of crystal violet doped droplets were laminated onto an ITO coated glass plate. This array was then exposed to the qualitative HCl sensitivity test in which they were exposed to closed atmospheres above concentrated HCl solutions. Subsequently, this array was then sandwiched between a second ITO coated glass plate and the absorption spectra recorded then an applied field was used to align the liquid crystal molecules. If HCl exposure produced a color change in the crystal violet dye indicators, this color

change would be most noticeable when the liquid crystal molecules are aligned by the applied field (i.e., the liquid crystal molecules are in a transmissive state). It was planned that this color change would be quantitatively measured by standard spectrophotometric absorption methods.

In fact, the results obtained did not support the use of the microencapsulated droplet dosimeter in that no color change was observed with these materials. This was true even on prolonged exposure of these droplets to relatively large vapor phase concentrations of HCl (i.e., over 500 ppm). We suspect this lack of dye sensitivity simply reflects the lack of permeability of HCl through the encasing HCl membrane. For example, we observed that a liquid pool of crystal violet/liquid crystals exhibited a rapid color change on exposure to these same HCl vapors.

In view of the above results, a decision was made to begin to explore alternative routes to passive badge HCl dosimetry which would eliminate the requirement for initial diffusion of HCl through a membrane barrier. As a result, the three types of dosimeter badges previously described were developed.

A total of nine indicator dyes were evaluated. Each of these nine dyes were fabricated in each of the three badge type configurations, namely adsorption on silica gel, incorporation into a PVA thin film and adsorption on a TLC strip. Qualitative testing for HCl sensitivity was as previously described, namely exposure to vapors of solutions containing varying concentrations of HCl. A summary of the results is presented in Table II.

In contrast with the situation observed with the microencapsulated droplets, all of the dye encoded samples exhibited easily observed color changes on exposure to HCl. As shown by the data in Table II, these dyes exhibited varying degrees of sensitivity towards the HCl as observed during our qualitative measurements.

As previously described, quantitative tests of these badge type HCl detectors were carried out by USABRDL scientists. The results communicated to us by these workers were as follows:

**Table II**  
**Evaluation of Dye Sensitivity for Use as Indicator in a Passive HCl Badge Dosimeter**

Polytronix Code	Dye Type	Original Color	Color After HCl Exposure	Transitional pH for Aqueous Solution	Indicator Response Sensitivity to HCl
D1	Bromothymol blue	Green	Orange	6.0 - 7.6	Most sensitive
D2	Bromphenol blue	Purple	Yellow	3.0 - 4.6	Very sensitive
D3	Bromocresol green	Dark blue	Orange	3.8 - 5.4	Very sensitive
D4	Bromocresol purple	Purple/brown	Orange	5.2 - 6.8	Most sensitive
D5	Congo red	Reddish brown	Blue	3.0 - 5.0	Very sensitive
D6	Methyl green	Blue	Yellow	0.6 - 1.7	Fairly sensitive
D7	Crystal violet	Purple	Yellow	0.5 - 1.7	Fairly sensitive
D8	Alizarin red	Pink	Yellow	6.0 - 7.0	Most sensitive
D9	Disulfonic acid*	Blue	Yellow	6.5 - 7.3	Most sensitive

\* The disulfonic acid employed was 2-(2,4-dinitrophenylazo)-1-naphthol-3,6-disulfonic acid disodium salt.

**TLC Strips:** Samples D2, D3 and D5 undergo a noticeable color change starting at a HCl concentration of 55 mg/m<sup>3</sup>. Sample D8 showed a slight color change at 400 mg/m<sup>3</sup> and a complete color change at 550 mg/m<sup>3</sup>.

**PVA Thin Films:** The PVA films for samples D1 through D6 showed no color change at HCl concentrations as high as 1400 mg/m<sup>3</sup>. Sample D8 did not change at 550 mg/m<sup>3</sup>.

**Silica Gel:** The only silica gel result reported was that of sample D9 which showed a color change at 400 mg/m<sup>3</sup>.

## Discussion

The rationale behind the use of acid-base indicators as a monitor for HCl is based on the dramatic color changes these materials undergo when exposed to certain changes in pH. If we consider the equilibrium system:



where HIn is a weak acid indicator molecule and  $\text{In}^-$  its conjugate base, then one can easily show that (Henderson-Hasselbalch equation):

$$\text{pH} = \text{pK}_a + \log \left[ \frac{(\text{In}^-)}{(\text{HIn})} \right] \quad (1)$$

The important physical property of these acid-base indicators is the marked difference in color between  $\text{In}^-$  and HIn. Indeed, it is this color difference which is the basis for the indicator action. As shown by equation I, the ratio of  $[\text{In}^-]/[\text{HIn}]$  in a given solution is a function of the pH of the solution. For example, for an indicator with a  $\text{pK}_a$  of 3.0, a variation of the pH of the solution from 2.0 to 4.0 results in a change in the ratio of  $[\text{In}^-]/[\text{HI}]$  from 1:10 to 10:1. Typically, such a 100-fold change in the ratio of the differently colored  $\text{In}^-$  and HIn species results in an easily observed color change. Furthermore, it is clear from equation I that in order to see clearly this color change, the solution pH must change by  $\text{pK}_a \pm 1$  to generate the 100-fold variation in molecular concentration.

In the current study, indicators of  $\text{pK}_a \leq 7.0$  were selected for evaluation. Indicators whose  $\text{pK}_a > 7.0$  would already be predominantly in the HIn form under typical atmospheric conditions and thus would not be able to undergo any further color change on exposure to HCl. The test data presented in Table II are in accord with the above discussion. The most sensitive detectors observed in our qualitative tests with freshly prepared samples are those whose  $\text{pK}_a$  values are in the range of 6.0 to 7.0 (i.e., samples D1, D4, D8 and D9). The second most sensitive class of indicators are those with  $\text{pK}_a$  values in range of 3.0 to 5.5 (i.e., D2, D3 and D5).

Finally, the least sensitive class are those with low  $pK_a$ 's of 0.5 to 1.7 (i.e., methyl green and crystal violet). Thus, it is clear that as the  $pK_a$  of the indicator decreases, exposure of the badges to ever-increasing concentrations of HCl is required in order to observe a color change.

In light of these results, the data from the quantitative tests at USABRDL are particularly important (and encouraging). The most sensitive detectors identified in these experiments were samples D2, D3 and D5, that is, the second most sensitive class as observed in our laboratories. We feel the difference in these two sets of data is easily resolved by noting that the Polytronix samples were analyzed immediately after preparation whereas those by USABRDL only after a significant time lapse (i.e., several weeks). During this time period between fabrication and eventual quantitative evaluations, exposure to atmospheric acids had, in all probability, already converted the most sensitive indicators (D1, D4, D8 and D9) to their acid forms. As a result, no further color change was noted by USABRDL personnel on exposure of these samples to HCl.

With respect to the above analysis, it is important to note that the medium sensitive samples (i.e., D2, D3 and D5) did exhibit good HCl sensitivity of around  $55 \text{ mg/m}^3$  in the quantitative test evaluations. Since the more sensitive samples (D1, D4, D8 and D9) exhibited at least an order of magnitude greater HCl sensitivity in our qualitative tests, it is clear that this dye indicator approach has the potential for development as a badge whose sensitivity would be in excess of the TLV of  $7 \text{ mg/m}^3$ . We feel this can be accomplished by providing these more sensitive indicators with a thin film protective layer which will eliminate (or at least minimize) the color change of these most sensitive dyes from the exposure to real atmospheres when not in use for HCl monitoring. There are a variety of ways in which this might be accomplished. In one format, the dosimeter would be fabricated into a completely sealed atmospheric impervious badge until ready for use. In use, this dosimeter would be activated by removal of a covering tape or plate on the front face of the badge. Obviously there are a large number of designs and configurations which could be explored in developing this type of badge. We would include initial sealing of the badge under an inert atmosphere to improve the shelf life of the dosimeter.

Alternately, we feel it is also possible to utilize the most sensitive dyes (e.g., D9) by manufacturing these devices under conditions in which the badge is assembled under inert atmosphere conditions and a thin film protective barrier applied to the indicator surface before atmospheric exposure. Specifically, we have in mind assembly in an inert atmosphere glove-box followed by application of a thin film RF plasma deposited coating. Polytronix has been very active in developing RF plasma coatings in recent years and we have recently been awarded a NSF SBIR phase II grant in this area (ref. 11). Using pulsed plasma deposition techniques, we have been able to produce a range of coatings including a number of perfluorocarbon films. The important advantages of the pulsed RF plasma techniques developed are that they provide exceptional control of film thickness, result in generation of pin-hole free coatings and provide a low temperature deposition mode for samples which may be temperature sensitive. Figure 1 is an example of the degree of film thickness control that is attainable using our pulsed RF plasma process with a perfluorocarbon (i.e.,  $C_3F_6$ ) monomer. The plasma deposited films obtained with certain fluorocarbon monomers exhibit a teflon-like structure as shown in Figure 2, as revealed by ESCA surface analysis. The large central peak in this figure is consistent with a dominant  $-CF_2-$  film surface. The teflon-like coating obtainable from perfluorocarbon RF plasma deposition is particularly relevant in view of the fact that HCl is known to have good penetration ability through teflon (ref. 12). Thus, we would visualize preparation of HCl badge dosimeters in which the most sensitive dyes would be employed and in which their acid induced color change would be retained. In this connection, we would note that our most sensitive dye, the disulfonic acid (D9), underwent a noticeable color change in the solvent evaporation step during exposure to normal atmospheres. We are confident that if this degree of sensitivity can be retained until deployment for HCl monitoring that detection limits would be achievable to well below the TLV level. Unlike the relatively thick barriers employed in our microencapsulation studies, the plasma thin film would have thicknesses in the range from perhaps 50 to 500 Å.

Finally, it is important to note that the dye indicator approach described in this work clearly has the potential for development as a true dosimeter and not simply as a detector. The dosimetry effect can be achieved by combining dyes of varying sensitivity into a single badge. Dye sensitivities could be selected to cover several orders of magnitude of HCl concentration ranges. For example, using the TLC plate badge types, small sections of TLC plates, each containing different dye indicators, could be laminated on a single substrate into a compact dosimeter. The dyes would be arranged in order of their varying dye sensitivities. After use, the dosimeter could be read by simple visual inspection or, more quantitatively, by reflectance spectroscopy. An additionally viable approach would be to simply modify the sensitivity of a particular dye indicator by using plasma deposited films of varying thickness. The variation of this membrane barrier thickness would result in a variation of the diffusion rate of HCl to the indicator surface and thus a dosimeter effect since the diffusion rate is proportional to the HCl concentration differential.

Based on the above considerations, we are confident that the basic acid-base dye indicator approach developed during this phase I project can be further extended in terms of its overall sensitivity. We hope to continue to explore this topic under a phase II project during which time a complete and functional passive HCl dosimeter meeting Army threshold value levels would be developed.

### Summation

During this phase I effort we have demonstrated the feasibility of employing dye indicators to signal the presence of atmospheric HCl. We have developed several promising physical dye adsorption approaches which have the potential for fabrication as simple, inexpensive dosimeter badges. The medium sensitivity dyes identified exhibit observable response to HCl at the 55 mg/m<sup>3</sup> level. The most sensitive dyes underwent atmospheric induced color changes before quantitative exposure to HCl was feasible. Since the most sensitive dyes are at least an order of magnitude more sensitive than the medium range dyes, it is clear that this approach has the



potential for development of dosimeter badges with sensitivity well below the Army threshold limit value of 7 mg/m<sup>3</sup>. The most sensitive dyes are those whose pKa's are in the range of 6.0 to 7.0. Their greater sensitivity is predicted by theory and was observed qualitatively in our laboratory tests.

We are confident that a continuation phase II effort on this project would result in the development of dye indicator based HCl dosimeters which will meet Army needs. This will be accomplished by stabilizing the most sensitive indicators against premature normal atmosphere induced color changes. Several promising routes to this stabilization have been identified in this report and they would form the focus of the proposed phase II effort.

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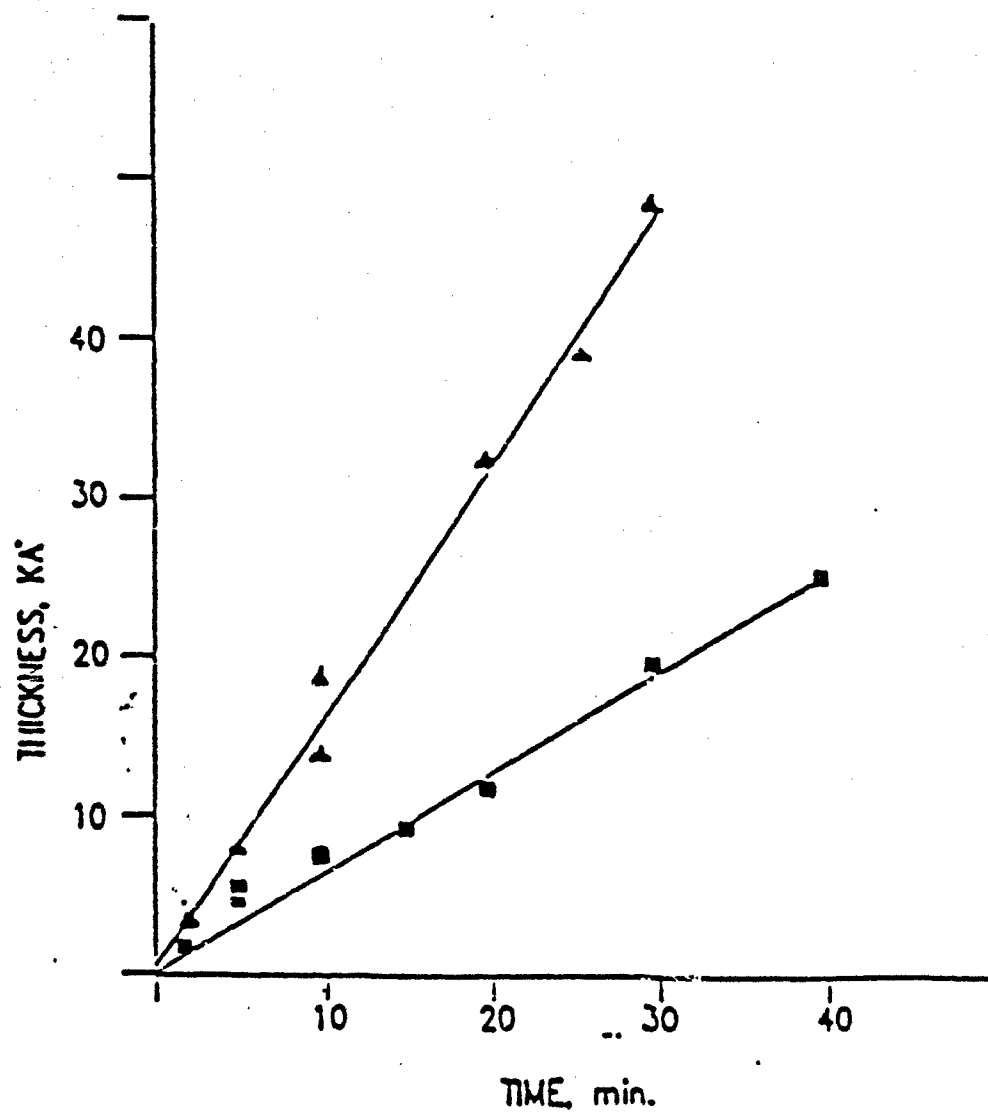


Figure 1. Demonstration of the film thickness control as a function of time during the pulsed plasma deposition of  $C_3F_6$  monomer.

- - RF plasma pulsed at 0.01 ms on / 0.02 ms off.
- ▲ - RF plasma pulsed at 1 sec on / 2 sec off.

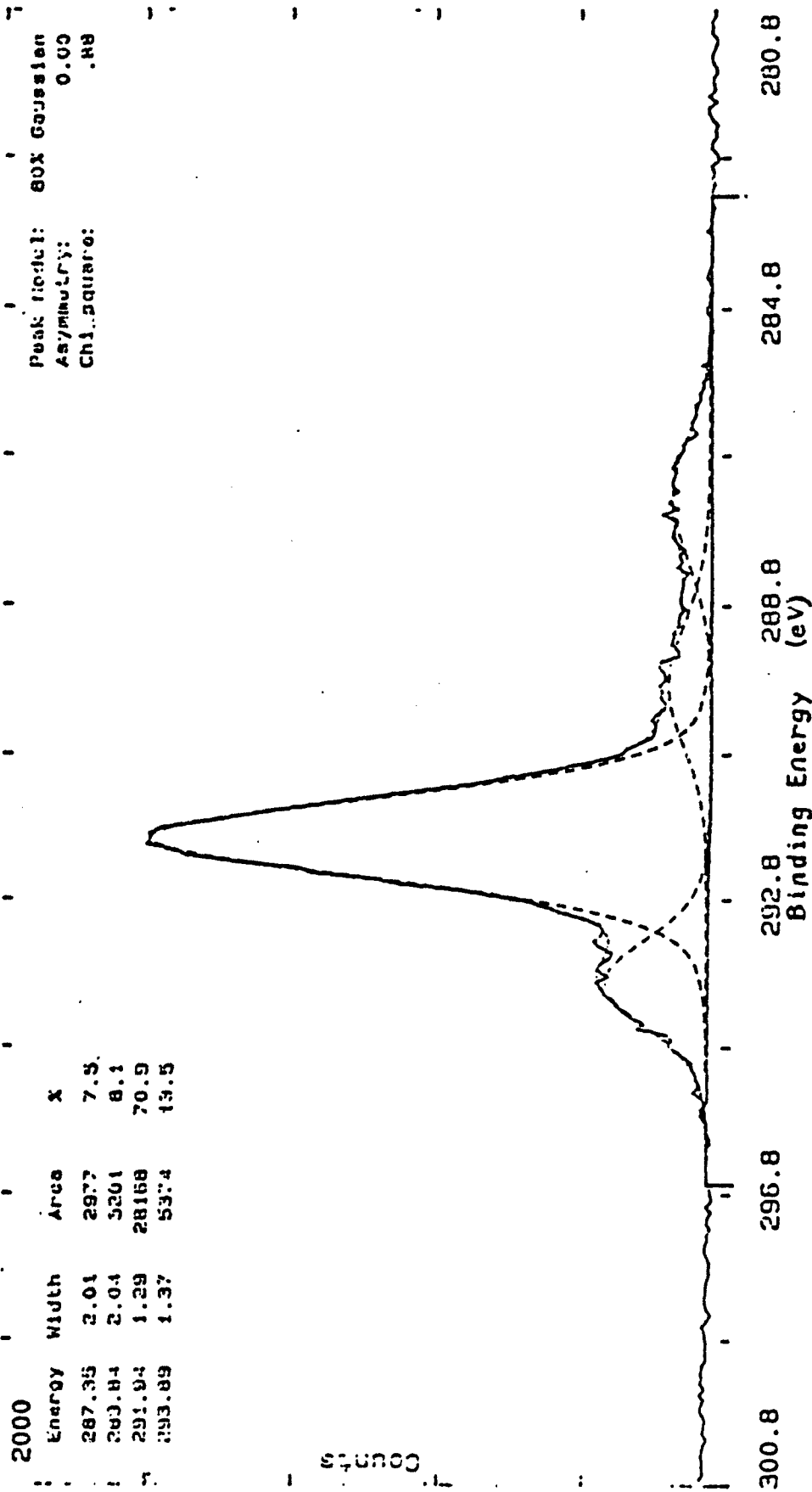


Figure 2. The high resolution C(1s) ESCA spectrum obtained during the pulsed RF plasma deposition of a perfluorocarbon monomer. The peaks at binding energies of 293.9, 291.9, 289.8 and 287.4 eV correspond to  $-\text{CF}_3$ ,  $-\text{CF}_2$ ,  $-\text{CF}$ , and  $-\text{C}-$  functionalities respectively. The surface composition is dominated by  $-\text{CF}_2$  groups.